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Dual impact of Nd³⁺ doping on CeO₂ abrasives: enhancing chemical and mechanical effects in chemical–mechanical polishing

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Abstract

As the demand for advanced optical glass technology increases, improving polishing slurries to enhance material removal rate and reduce surface roughness has become a priority. Cerium oxide is the most widely used abrasive for glass polishing, and its polishing rate is regarded to increase as the surface Ce³⁺ content rises. To improve this, Nd³⁺-doped cerium oxide was prepared using a molten salt method. Morphological and X-ray photoelectron spectroscopy (XPS) analyses showed that the Nd³⁺ doping increased Ce³⁺ content and transformed the particles into an octahedral structure. Additionally, Nd³⁺ doping enhanced the mechanical action, as evidenced by an increased friction coefficient and reduced contact angle. When the doping amount is 4%, Ce³⁺ content and material removal rate peaked at 47.87 nm/min, while the doping amount is 8%, mechanical and chemical synergy achieved the lowest surface roughness of 1.38 nm.

Keywords Chemical mechanical polishing, CeO₂, Doping, Glass substrate

1 Introduction

Chemical mechanical polishing (CMP) technology's development stems from the need for higher surface flatness and smoothness in shrinking semiconductor sizes, smooth transitions between layers in multilayer integrated circuits, and the removal of defects and contaminants to meet stringent surface quality requirements. As integrated circuit sizes shrink, achieving precise planarization becomes essential to reduce defects and optimize the performance of the devices. CMP enables the production of smaller, more complex devices with higher packing densities and improved functionality. These factors collectively drive the advancement of CMP technology

in semiconductor manufacturing [1–3]. CMP is a sophisticated technique that achieves precise surface flatness by concurrently considering local and global material aspects [4]. The process combines mechanical abrasion and chemical reactions, with the polishing slurry playing a critical role in influencing material removal rates, surface finishes, and preventing damage to delicate semiconductor structures. The polishing slurry playing a key role in influencing performance and efficiency [5]. The continued advancement of CMP technology is crucial for ensuring the performance and reliability of semiconductor devices, contributing to the development of more powerful and energy-efficient devices.

In these slurries, abrasives exert both mechanical and chemical effects on the workpiece, thereby directly influencing the outcomes of the CMP process [5–7]. CeO₂ has moderate hardness and good mechanical action, while it has chemical tooth effect and significant chemical activity [8], which make it widely suitable for chemical mechanical polishing in various products including optical glass [9]. Cerium's ability to exist in various valence

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states and readily switch between them facilitates complexing of SiO_2 , solidifying CeO_2 as an effective polishing abrasives [10]. Sabia and Stevens discovered that during the polishing process, both Ce^{4+} and Ce^{3+} were present on the surface of CeO_2 abrasive particles [11]. Xu et al. demonstrated that enhancing the ratio of Ce^{3+} could improve the CeO_2 abrasives' polishing efficiency [12]. Schmidt et al. found that trivalent ion doping enhances Ce^{3+} formation on CeO_2 crystals [13]. Similarly, Patil et al. found that trivalent ion doping creates many oxygen vacancies in CeO_2 without altering its structure [14]. Cheng et al. experimented with lanthanide doping (La, Nd, Yb) on commercial CeO_2 abrasives, resulting in a notable enhancement in the abrasives' polishing efficiency on SiO_2 matrices [15]. Jin et al. reported a significant increase in the polishing efficiency of CeO_2 abrasives with high Nd^{3+} doping, showing a 3.62-fold higher rate compared to pure CeO_2 [16]. These studies have confirmed the potential of Nd^{3+} doping to enhance MRR.

However, Cheng and Jin et al. utilized surface immersion and hydrothermal methods for doping, which are commonly used in the synthesis of CeO_2 . While the salt melting method has been applied in various contexts, its specific advantages for CeO_2 synthesis were further demonstrated by Xia's research [17], which showed that CeO_2 prepared using the crucible-based salt melting method exhibited a higher Ce^{3+} concentration. The salt melting method has gained significant attention for its environmentally friendly nature, cost-effectiveness, simplicity, and scalability in producing nanomaterials with diverse chemical compositions and morphologies. This technique employs molten salts as a reaction medium to facilitate the dissolution and recrystallization of precursors at elevated temperatures, allowing precise control over particle size and morphology under moderate reaction conditions. In the case of CeO_2 synthesis, salt melting method offers distinct advantages over the hydrothermal method. Unlike the latter, salt melting method operates at lower internal pressures during the reaction, reducing the likelihood of Ce^{3+} oxidation by oxygen and water vapor. This results in a higher surface concentration of Ce^{3+} , a factor that significantly enhances the material's properties and contributes to improved MRR, as confirmed by Xia's findings. Additionally, Ma et al. investigated Y^{3+} , La^{3+} , and Pr^{3+} doping of CeO_2 by the salt melting method and found that Y^{3+} doped CeO_2 exhibited the highest Ce^{3+} concentration and MRR [18]. Furthermore, Xu et al. enhanced MRR by preparing Y^{3+} doped $\text{Ce}_{1-x}\text{Y}_x\text{O}_2$ particles and polishing quartz glass under photocatalysis [19]. These studies have conducted extensive research on the synthesis of cerium oxide and provided a detailed explanation of its chemical mechanisms. However, chemical mechanical polishing

involves not only chemical interactions but also significant mechanical actions and the wetting effects of the polishing slurry. These aspects were not addressed in the previous research by Ma and Xu et al. Specifically, their conclusions regarding the mechanical actions lack a solid theoretical foundation. Therefore, further testing of its mechanical properties is required.

In this work, the abrasives $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ with different doping amounts were synthesized using the molten salt method (x is the doping amount of Nd^{3+} in CeO_2 , $x=0.00, 0.02, 0.04, 0.06, 0.08, 0.10$). The chemical and mechanical effects of CMP were investigated, and a mechanism for CMP was proposed.

2 Experimental and methods

2.1 Preparation of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives

The abrasives $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ with different doping amounts were synthesized using the molten salt method [18] (x is the doping amount of Nd^{3+} in CeO_2 , $x=0.00, 0.02, 0.04, 0.06, 0.08, 0.10$). However, it is worth noting that the reaction temperature was optimized (800°C) to ensure that the particle size remained in a suitable range.

2.2 Characterization of the abrasives and polishing slurry

The descriptions of the characterization details are reported in the supporting information (S1).

2.3 CMP experiment

The preparation method for the CMP polishing slurry is as follows: adding the abrasive to deionized water ($\text{PH}=10$), dispersing it with ultrasonic waves for 10 min, stirring with a magnetic agitator for 5 min, and then conducting the CMP test. The experimental details are shown in Table 1.

After polishing, MRR is calculated by Eq. (1) [18, 20]:

Table 1 Polishing process details

Parameter	Specification
Polishing machine	UNIPOL-1000S, Shenyang Kejing Instrument Co., LTD., China
Polishing time	3 min
Polishing load	3.5 kg
Platen's rotation speed	80 r/min
Carrier's rotation speed	80 r/min
Polishing slurry: Solid content	$\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasive 1.5 g (0.5wt %)
Polishing slurry: Solvent content	deionized water 300 ml ($\text{PH}=10$)
Polished substrate	pristine soda lime glass (diameter 50 mm)
polishing pad	Rodel porous polyurethane pad

$$MMR = \frac{\Delta m \cdot 10^4}{\rho \pi R^2 \tau} \quad (1)$$

MRR: Material removal rate (nm/min); Δm : The material mass (g) removed from the glass substrate during polishing, obtained by calculating the quality difference of the glass substrate before and after polishing. The quality of the glass substrate before and after polishing was obtained by acetone cleaning and drying and weighing. R: substrate radius (cm); τ : Polishing time (min); ρ : Density of substrate ($\rho_{\text{glass}} = 2.5 \text{ g/cm}^3$).

3 Results and discussions

3.1 Phase and morphology analysis

The XRD pattern of $\text{Ce}_{0.9}\text{Nd}_{0.1}\text{O}_2$ abrasive and CeO_2 abrasive are shown in Fig. 1. The diffraction peaks of CeO_2 are located at 2θ values of approximately 28.6° , 33.2° , 47.6° , 56.4° , 59.2° , 69.5° , 76.7° , and 79.1° . These peaks correspond to the (111), (200), (220), (311), (222), (400), (331), and (420) planes of the CeO_2 phase, as referenced in PDF#04-002-3313. For $\text{Ce}_{0.9}\text{Nd}_{0.1}\text{O}_2$, the diffraction peaks are observed at 2θ values around 28.5° , 33.1° , 47.5° , 56.3° , 59.1° , 69.4° , 76.7° , and 79.1° , which are also associated with the (111), (200), (220), (311), (222), (400), (331), and (420) planes of the CeO_2 phase, according to the same reference. Comparing the diffraction peaks of $\text{Ce}_{0.9}\text{Nd}_{0.1}\text{O}_2$ with CeO_2 , it is evident that Nd^{3+} doping does not notably shift the overall peak positions of cerium oxide, confirming that it remains in the cerium oxide phase without the appearance of impurity peaks related to Nd, thus confirming the successful doping. In

the XRD pattern of $\text{Ce}_{0.9}\text{Nd}_{0.1}\text{O}_2$, the larger radius of Nd^{3+} (99.5 pm) compared to Ce^{4+} (92 pm) [21] causes lattice expansion in CeO_2 , resulting in a peak shift [18] towards lower angles.

The shape and size of abrasives significantly impact the mechanical effectiveness in CMP processes. Figure 2(a)-(f) displays SEM images of CeO_2 abrasive and $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives. As shown in Fig. 2(a), the CeO_2 abrasive particles have a polyhedral shape with an average size of 534 nm. In contrast, Fig. 2(b)-(g) illustrate that the particle size of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasive is all smaller than CeO_2 , and the particle size decreases with increasing of Nd^{3+} doping levels. As the particle size decreases, the depth to which the abrasive penetrates the substrate material during the polishing process is reduced, leading to a decrease in the mechanical action. Alternatively, the shape of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives transitions from polyhedral to octahedral as the Nd^{3+} doping increases, maintaining a primarily octahedral structure when the doping level reaches 4%. The octahedral shape, with its sharper edges compared to those of polyhedral shapes, generates greater point pressure during the polishing process, thereby increasing the material removal rate from the substrate. Figure 3 (a)-(b) shows the EDS spectra of CeO_2 abrasive and $\text{Ce}_{0.9}\text{Nd}_{0.1}\text{O}_2$ abrasive. Only Ce and O elements exist in the EDS results of CeO_2 abrasive, while Ce, O and Nd elements exist in $\text{Ce}_{0.9}\text{Nd}_{0.1}\text{O}_2$ abrasives, which also confirms the success of Nd^{3+} doping [18].

The zeta potential method measures system stability [22], a higher absolute zeta potential implies increased repulsive forces between particles, leading to greater

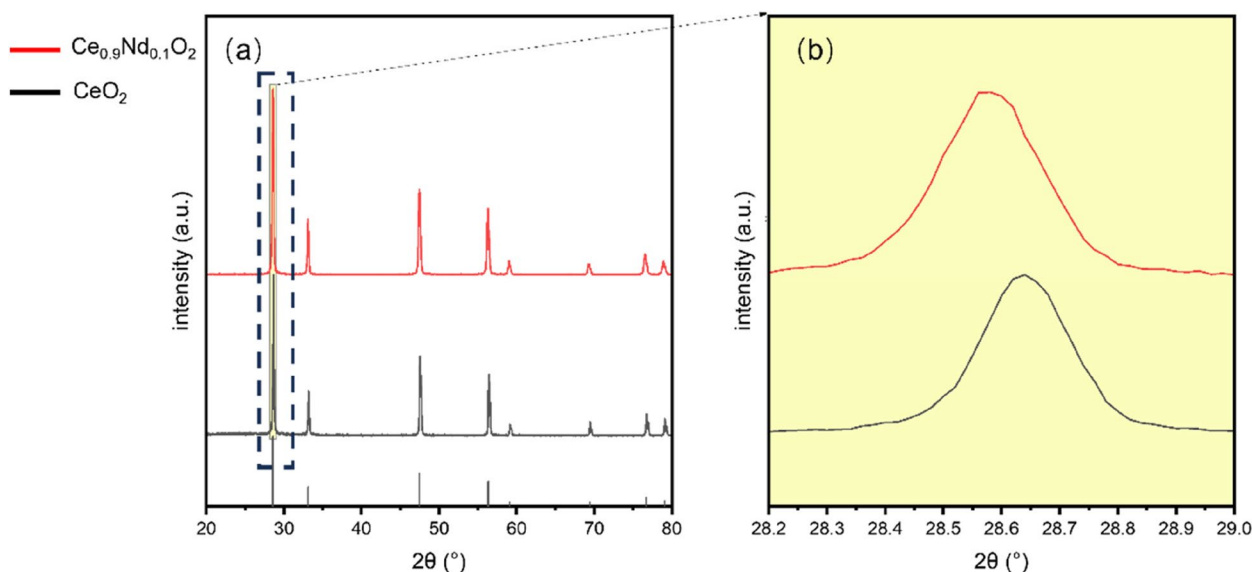


Fig. 1 a XRD pattern of prepared CeO_2 and $\text{Ce}_{0.9}\text{Nd}_{0.1}\text{O}_2$ (compared with CeO_2 standard PDF cards, b Partially enlarged view of the XRD pattern shown in (a))

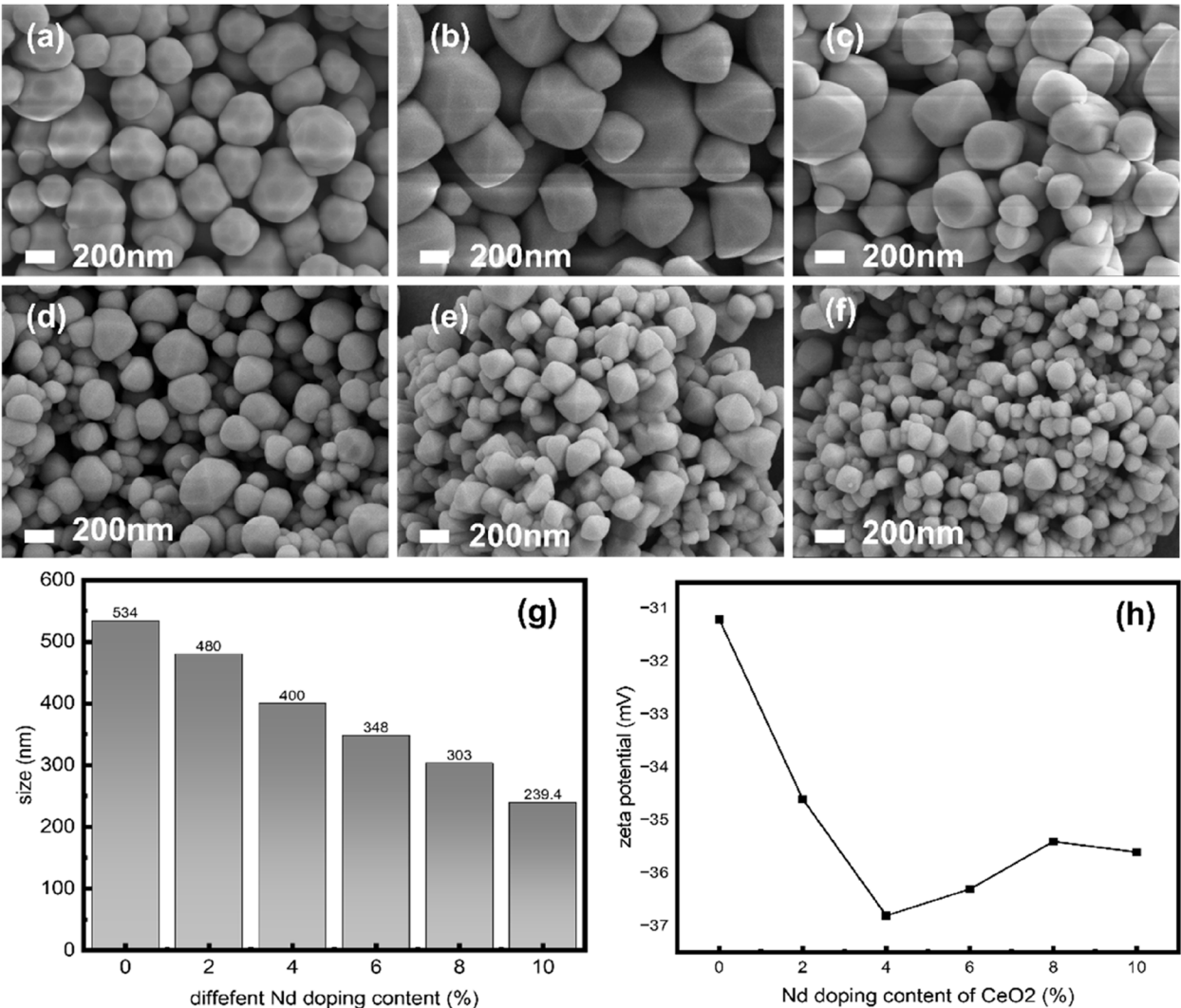


Fig. 2 SEM images of $Ce_{1-x}Nd_xO_2$ abrasives (x is the content of Nd^{3+} doping in CeO_2 , $x =$ (a) 0%, (b) 2%, (c) 4%, (d) 6%, (e) 8%, (f) 10%), (g) particle size of $Ce_{1-x}Nd_xO_2$ abrasives and (h) zeta potential of $Ce_{1-x}Nd_xO_2$ polishing slurry

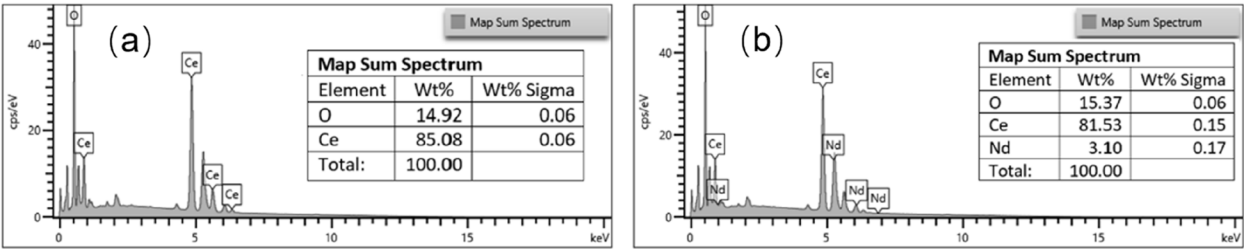


Fig. 3 EDS spectra of (a) pure CeO_2 abrasive and (b) $Ce_{0.9}Nd_{0.1}O_2$ abrasive

stability. Generally, a zeta potential above 30 mV indicates a more stable suspension [23]. Figure 2(h) shows that the zeta potential of polishing slurry prepared by CeO_2 abrasive is -31.2 mV, indicating that the polishing

slurry made from CeO_2 prepared by this method is relatively stable. Furthermore, the absolute zeta potential of the polishing slurries prepared with doped $Ce_{1-x}Nd_xO_2$ abrasives is higher than CeO_2 abrasive. This indicates

that Nd^{3+} doping enhances the stability of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives polishing slurries. When the doping amount is 4%, the absolute zeta potential is at its highest, suggesting that the polishing slurry exhibits the greatest stability.

3.2 Surface defect analysis

Figure 4(a) presents the XPS spectrum of the CeO_2 abrasive and $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives. The spectrum for CeO_2 abrasive reveals the presence of only Ce and O elements, with no detectable K, Na, Cl, or Nd elements. Conversely, the spectrum for $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives reveals the presence of Ce, Nd, and O elements, but no K, Na, or Cl elements. The absence of detectable K, Na, Cl elements in both the CeO_2 abrasive and $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives indicating that no residual salts are present on the surface. Additionally, peaks observed in the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives spectrum at 982.3 eV and 1005.8 eV correspond to Nd $3d_{3/2}$ and Nd $3d_{5/2}$, respectively. The results confirm Nd^{3+} ions are located at the surface of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives. Combined with XRD and EDS results, it is evident that Nd^{3+} ions are successfully doped in the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives.

As Ce^{3+} is a key factor in the polishing process of CeO_2 surfaces, The Ce 3d characteristic spectrum is analyzed, with the spin-orbitals $3d_{5/2}$ and $3d_{3/2}$ represented by the symbols "v" and "u," respectively. The peaks corresponding to Ce^{3+} are marked as v_o , v' , u_o , and u' , whereas the peaks for Ce^{4+} are labeled v , v'' , v''' , u , u'' , and u''' [19]. The final XPS fitting results are shown in Fig. 4(b)-(g), with more detailed peak area data and binding energies provided in Table 2. The Ce^{3+} concentration of CeO_2 and $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives was calculated using Eqs. (2)-(4), and the results are shown in Fig. 4(h). The findings indicate that the Ce^{3+} concentration of CeO_2 abrasive surface is only 22.51%, while the Ce^{3+} concentration of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasive surface is higher. Specifically, the $\text{Ce}_{0.96}\text{Nd}_{0.04}\text{O}_2$ abrasive surface exhibited the highest Ce^{3+} concentration, at 37.68%.

$$C(\text{Ce}^{3+}) = \frac{A(\text{Ce}^{3+})}{A(\text{Ce}^{3+}) + A(\text{Ce}^{4+})} \quad (2)$$

$$A(\text{Ce}^{3+}) = A(V_o) + A(V') + A(U_o) + A(U') \quad (3)$$

$$A(\text{Ce}^{4+}) = A(V) + A(V'') + A(V''') + A(U) + A(U'') + A(U''') \quad (4)$$

Additionally, the oxygen vacancy content on CeO_2 abrasive was found to correlate positively with the Ce^{3+} content. The O 1s characteristic spectrum was examined, as shown in Fig. 5(a)-(f). The peaks at 529 eV, 531 eV, and 533 eV correspond to lattice oxygen ($\text{O}\alpha$),

surface oxygen ($\text{O}\beta$), and adsorbed oxygen ($\text{O}\gamma$), respectively [24]. Here, $\text{O}\beta$ represents the oxygen vacancy present in the CeO_2 abrasive, which can be calculated by Eq. (5). Calculated oxygen vacancy concentration of the CeO_2 and $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasive surface are shown in Fig. 5(g). The results show that the oxygen vacancy concentration on the CeO_2 abrasive surface is 34.44%, whereas it is higher on the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasive surface. Specifically, the $\text{Ce}_{0.96}\text{Nd}_{0.04}\text{O}_2$ abrasive surface exhibits the highest surface oxygen vacancy concentration (45.20%). This indicates that more Ce^{4+} is reduced to Ce^{3+} in the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ crystal, aligning with the calculated Ce^{3+} concentration.

$$C(\text{oxygen vacancy}) = \text{O}\beta / (\text{O}\alpha + \text{O}\beta + \text{O}\gamma) \quad (5)$$

Furthermore, Raman spectroscopy was employed to further verify the presence of oxygen vacancies on CeO_2 abrasives. As depicted in Fig. 6. The peak around 460 cm^{-1} represents the $\text{F}2\text{g}$ vibration mode of cubic CeO_2 [25], while the peak at 600 cm^{-1} indicates doping-related structural defects [21]; the ratio of these peak intensities (I_{600}/I_{460}) reflects the concentration of oxygen vacancies in CeO_2 [26], as shown in Eq. (6):

$$C(\text{oxygen vacancy}) = (I_{600}/I_{460}) \quad (6)$$

The oxygen vacancy concentration is 0.58% for CeO_2 abrasives and higher for $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives, with $\text{Ce}_{0.96}\text{Nd}_{0.04}\text{O}_2$ showing the highest at 3.39%. This indicates more Ce^{4+} is reduced to Ce^{3+} , consistent with both XPS and Raman spectroscopy results.

3.3 Contact angle analysis

The effect of Nd^{3+} doping on the surface hydrophilicity of polishing slurries prepared with CeO_2 abrasives and $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives was further investigated. Static contact angles between polishing slurries prepared by CeO_2 abrasive and $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives and glass substrates were measured by a contact angle measurement instrument, as shown in Fig. 7. The contact angle between pure water and the glass substrate is 48.3° . However, the contact angle between the polishing slurries and the glass substrate decreases with the addition of CeO_2 abrasive and $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives. The minimum contact angle observed was 22.6° , which was obtained with polishing slurries prepared by $\text{Ce}_{0.96}\text{Nd}_{0.04}\text{O}_2$ abrasive. These results indicate that Nd^{3+} doping can improve the hydrophilicity of polishing slurries prepared by CeO_2 abrasive and $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives. When the doping amount is 4%, the contact angle reaches its minimum. This matches the XPS results, showing that the higher Ce^{3+} concentration on the $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ improves bonding with the SiO_2 in the glass substrate. Therefore, it is

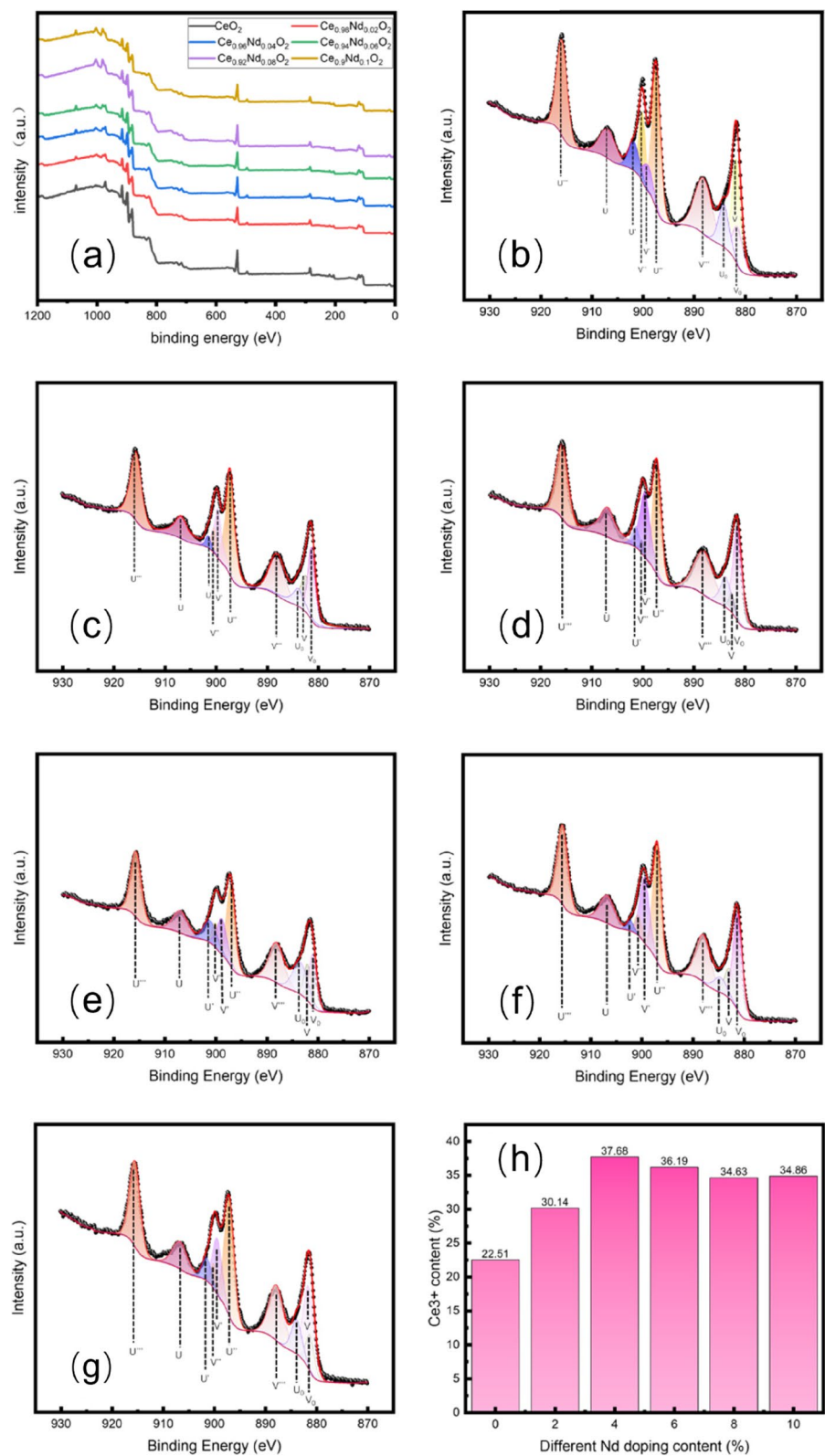


Fig. 4 XPS spectra of abrasives: **(a)** Survey of CeO₂ and Ce_{1-x}Nd_xO₂; **(b-d)** Ce 3d spectra of CeO₂, Ce_{0.98}Nd_{0.02}O₂, Ce_{0.96}Nd_{0.04}O₂, **e-g** Ce 3d spectra of Ce_{0.94}Nd_{0.06}O₂, Ce_{0.92}Nd_{0.08}O₂, Ce_{0.9}Nd_{0.1}O₂ respectively; **(h)** Ce³⁺ concentration of the CeO₂ and Ce_{1-x}Nd_xO₂ abrasive surface

Table 2 The binding energies and peak areas for the abrasives

	Ce ³⁺				Ce ⁴⁺						Ce ³⁺ content
	V ₀	V'	U ₀	U'	V	V''	V'''	U	U''	U'''	
CeO ₂											
BE (eV)	881.47	899.11	884.22	901.82	881.85	900.18	888.21	906.93	897.45	915.90	
Area	18720	12770	21068	14372	40793	22666	43956	21555	55225	46152	22.51%
Ce _{0.98} Nd _{0.02} O ₂											
BE (eV)	881.36	899.64	883.95	901.55	882.47	900.39	888.08	906.87	897.28	915.67	
Area	25616	25390	12517	3002	25898	6052	27011	18609	43444	34901	30.14%
Ce _{0.96} Nd _{0.04} O ₂											
BE (eV)	881.44	899.55	883.72	901.32	882.58	900.18	888.00	906.90	897.21	915.77	
Area	41357	33435	15434	7382	5566	2257	39078	28881	42239	40045	37.68%
Ce _{0.94} Nd _{0.06} O ₂											
BE (eV)	881.01	898.79	883.47	901.07	882.02	900.05	888.09	906.94	897.04	915.65	
Area	19485	17704	22392	13932	12500	8257	27638	15228	32380	32418	36.19%
Ce _{0.92} Nd _{0.08} O ₂											
BE (eV)	881.26	899.43	884.64	902.24	882.86	900.66	887.98	906.77	897.00	915.51	
Area	41854	30720	8929	3375	13569	7376	32519	19135	46112	39321	34.63%
Ce ₀ Nd _{0.1} O ₂											
BE (eV)	881.60	899.41	883.86	901.46	881.24	900.14	887.85	906.74	897.10	915.57	
Area	29594	19009	12245	7382	10427	4926	27890	13728	38469	30847	34.86%

reflected at the macro level that the polishing slurries exhibits lower contact angle performance. In the CMP process, the contact angle between the slurry and the glass substrate plays a key role in both the chemical and mechanical actions of the polishing process. A smaller contact angle leads to a higher diffusion coefficient of the slurry on the glass surface, increasing the contact area. Consequently, a reduced contact angle allows the effective substances in the slurry to diffuse more efficiently to the glass surface during polishing, enhancing the chemical reaction at the interface and may improving the SiO₂ removal rate [27]. Additionally, a smaller contact angle increases the mechanical interaction by enlarging the contact area, thereby enhancing the abrasion effect. Conversely, if the contact angle between the polishing liquid and the glass substrate increases, it would reduce the diffusion of active substances to the wafer surface and decrease the contact area, thereby diminishing both the chemical reaction and the mechanical abrasion efficiency, ultimately may lowering the SiO₂ removal rate. This offers a more intuitive understanding of the mechanical behavior of doped cerium oxide polishing slurry.

3.4 Friction coefficient

In the CMP process, mechanical action is crucial for material removal. It relies on both chemical reactions and mechanical wear. Greater mechanical forces lead to increased contact pressure, enhancing the abrasive particles' wear effect on the material surface [28]. A higher

coefficient of friction results in greater friction under the same normal force. This increased friction enhances the scraping and cutting actions of the abrasive particles on the material surface, thereby improving wear efficiency. Consequently, more material can be removed per unit time. The dynamic friction coefficient (COF) of CeO₂ and Ce_{1-x}Nd_xO₂ abrasives was measured using a friction coefficient meter. According to Fig. 8, pure CeO₂ has the lowest average COF at 0.37. In contrast, the COF of Ce_{1-x}Nd_xO₂ abrasives doped with Nd³⁺ is higher. Notably, when the Nd³⁺ doping amount is 4%, the dynamic COF reaches its maximum value of 0.42. This may be due to the improved adhesion between the polishing particles and the SiO₂ in the glass substrate. More bonding leads to increased polishing resistance. This is also consistent with XPS and contact angle changes. When the doping amount is 4%, the abrasive particles have the highest surface Ce³⁺ concentration, allowing for better bonding with the SiO₂. Simultaneously, the polishing particles achieve greater contact with the glass substrate, facilitating increased bonding between abrasive and the substrate. Consequently, polishing resistance and the COF increase. However, in the previous XPS analysis, with Nd³⁺ doping at 6%, the surface Ce³⁺ content was found to be less than 4%. Interestingly, despite both samples exhibiting an octahedral morphology, the COF remained identical to that of the 4% doping level. The primary distinction lay in the size of the abrasives: 400 nm for the 4% doping and 348 nm for the 6% doping. This observation suggests that

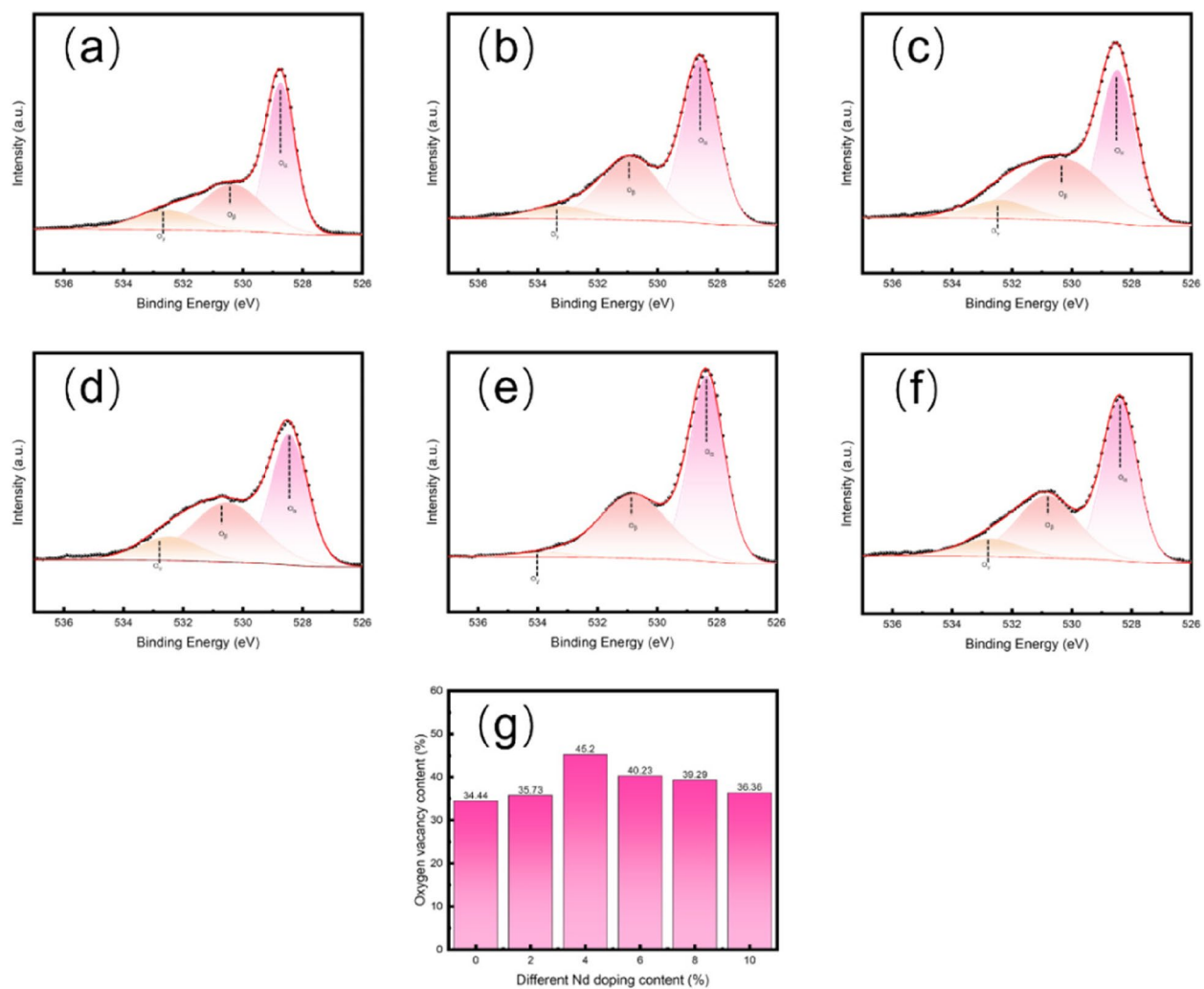


Fig. 5 XPS spectra of CeO_2 abrasives (a–g) O 1s spectra of CeO_2 , $\text{Ce}_{0.98}\text{Nd}_{0.02}\text{O}_2$, $\text{Ce}_{0.96}\text{Nd}_{0.04}\text{O}_2$, $\text{Ce}_{0.94}\text{Nd}_{0.06}\text{O}_2$, $\text{Ce}_{0.92}\text{Nd}_{0.08}\text{O}_2$, $\text{Ce}_0\text{Nd}_{0.1}\text{O}_2$ respectively; (h) Oxygen vacancy concentration of the CeO_2 and $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasive surfaces

at an abrasive size of 348 nm, there is improved contact between the abrasive particles and the glass substrate, which compensates for the lower Ce^{3+} content and enhances their adhesion. This underscores the critical role of particle size in mechanical interactions.

3.5 Material removal rate (MRR) analysis

Improved material removal rates contribute to saving processing time and reducing abrasive costs. Therefore, achieving high material removal rates is a common goal in the industry [29]. Figure 9 shows that the MRR for glass substrates polished with $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives ranges from 35.99 to 47.87 nm/min, significantly higher than the 28.18 nm/min of CeO_2 abrasives. Nd^{3+} doping improves polishing efficiency, with $\text{Ce}_{0.96}\text{Nd}_{0.04}\text{O}_2$ showing the highest MRR, 69.88% greater than pure CeO_2 . This enhancement is due to better bonding between the

abrasive and SiO_2 and the effective mechanical action of larger, polyhedral particles when doping is under 4%. However, the MRR does not peak due to low chemical activity. At low doping levels, the abrasive's chemical activity is the primary factor affecting MRR. Reduced chemical activity limits bonding between abrasive particles and the glass substrate, resulting in inadequate SiO_2 removal and a lower MRR.

When the doping amount is 4%, the Ce^{3+} concentration on the surface of the abrasive reaches its highest level, resulting in the strongest chemical interaction during the polishing process. This enhances the formation of chemical bonds between the abrasive particles and SiO_2 , allowing for more efficient removal of SiO_2 fragments from the substrate material. At this doping level, the morphology of the abrasives transitions to an octahedral shape, which further enhances the mechanical action during polishing.

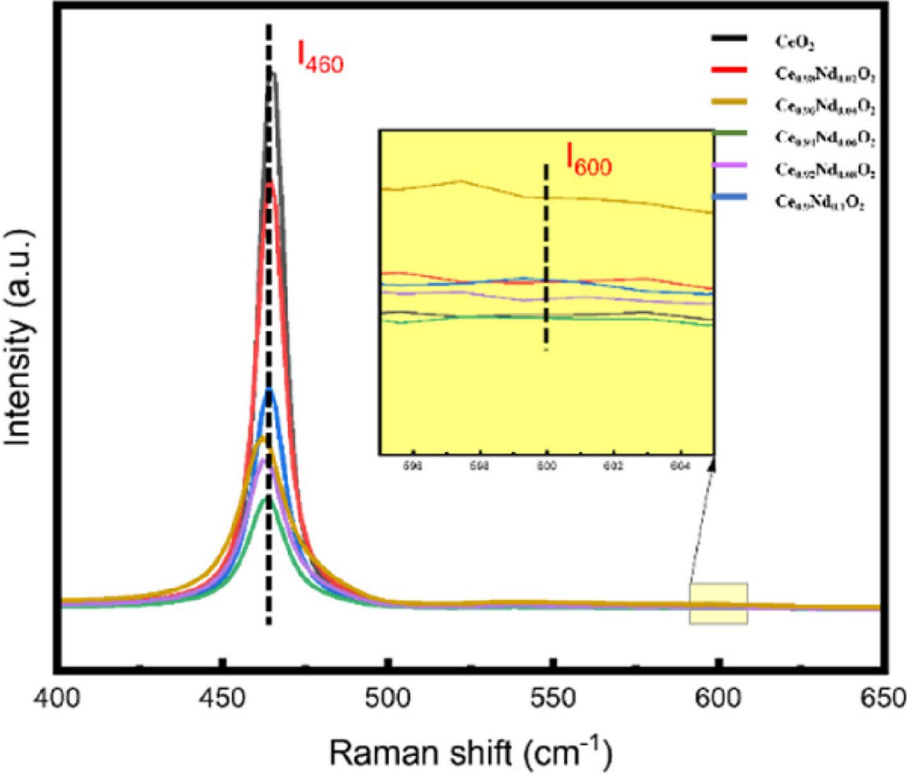


Fig. 6 Raman spectra of CeO_2 and $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$

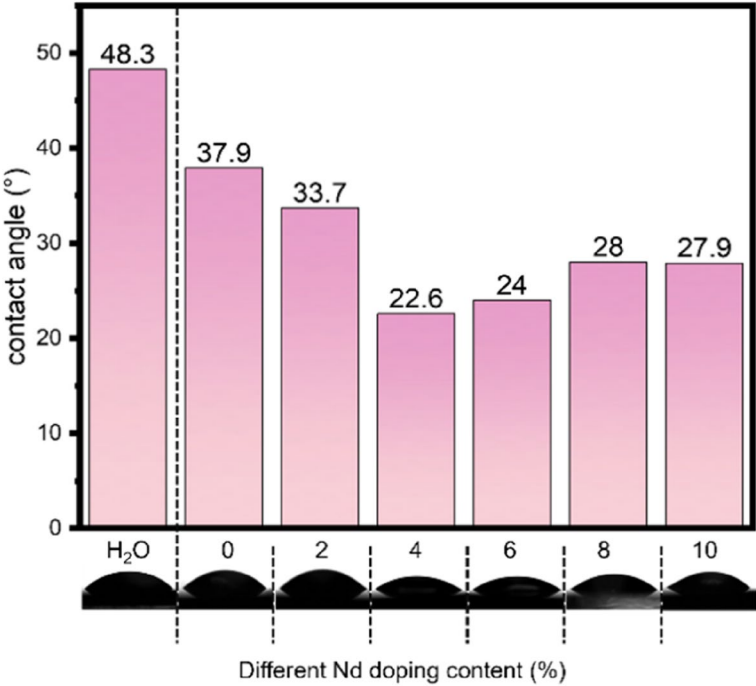


Fig. 7 The contact angle of CeO_2 and $\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ slurries on glass substrate

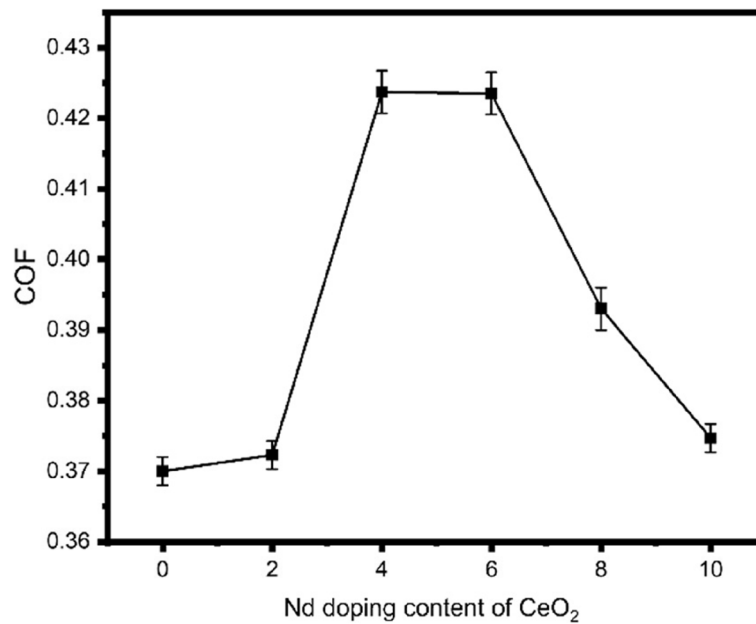


Fig. 8 Coefficient of friction vs. different Nd³⁺ doping contents

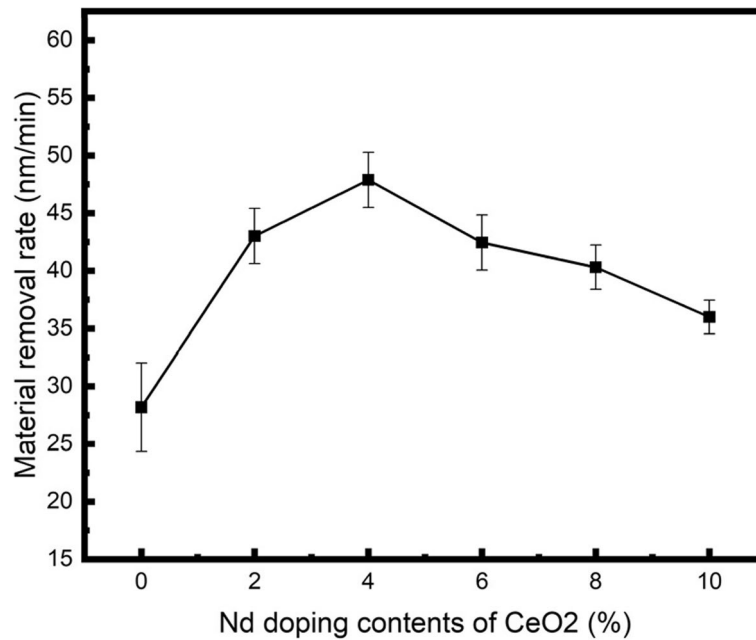


Fig. 9 Curve of material removal rate with doping amount

The octahedral particles, with sharper edges compared to the polyhedral shape, generate higher localized pressure on the substrate when subjected to the same external force. This increased pressure facilitates the detachment of SiO₂ fragments from the substrate surface. Although the reduction in particle size due to doping leads to a decrease in the mechanical action and the depth of

particle penetration into the substrate, the overall material removal rate is highest at a doping amount of 4%. However, when the doping amount exceeds 4%, the Ce³⁺ concentration of the particles begins to decrease, leading to a reduction in chemical action. Although the abrasives have stabilized into an octahedral shape with good mechanical effect, the abrasive size is reduced, causing

some abrasives to become embedded in the polishing pad, thereby diminishing their effective polishing capability. Especially When doping reaches 8% or 10%, although the Ce^{3+} concentration of the abrasive is higher than at 2%, the MRR decreases. This is due to the reduced particle size, which weakens the bonding between the abrasive particles and SiO_2 and diminishes mechanical action, leading to a lower MRR.

3.6 Surface quality analysis of polished and unpolished glass substrates

Surface roughness is a key factor influencing both the functional performance and the overall quality of a glass substrate. For instance, in applications involving optical devices, lenses, or optical systems, surface roughness contributes to light scattering, diffuse reflection, and optical distortion, consequently diminishing transparency, imaging precision, and overall optical performance

[4]. Hence, within the CMP process, precise assessment and meticulous management of surface roughness stand as indispensable measures to uphold product excellence, ensure device reliability, and maintain process stability. Figure 10. illustrates the surface profile of the unpolished and polished glass substrate with CeO_2 and $Ce_{1-x}Nd_xO_2$. Compared to the high roughness of the unpolished glass substrate ($S_a=3.12$ nm), the glass surfaces polished with CeO_2 and $Ce_{1-x}Nd_xO_2$ slurries appear smoother and free of noticeable bumps. Figure 11 highlights the surface roughness of glass substrates polished with different abrasives, showing that $Ce_{1-x}Nd_xO_2$ achieves lower roughness than CeO_2 . Notably, the glass substrate polished with $Ce_{0.92}Nd_{0.08}O_2$ has the lowest roughness ($S_a=1.38$ nm).

Based on these findings, several observations have emerged. First of all, the glass substrates polished by polishing slurries prepared by $Ce_{0.92}Nd_{0.08}O_2$ abrasive

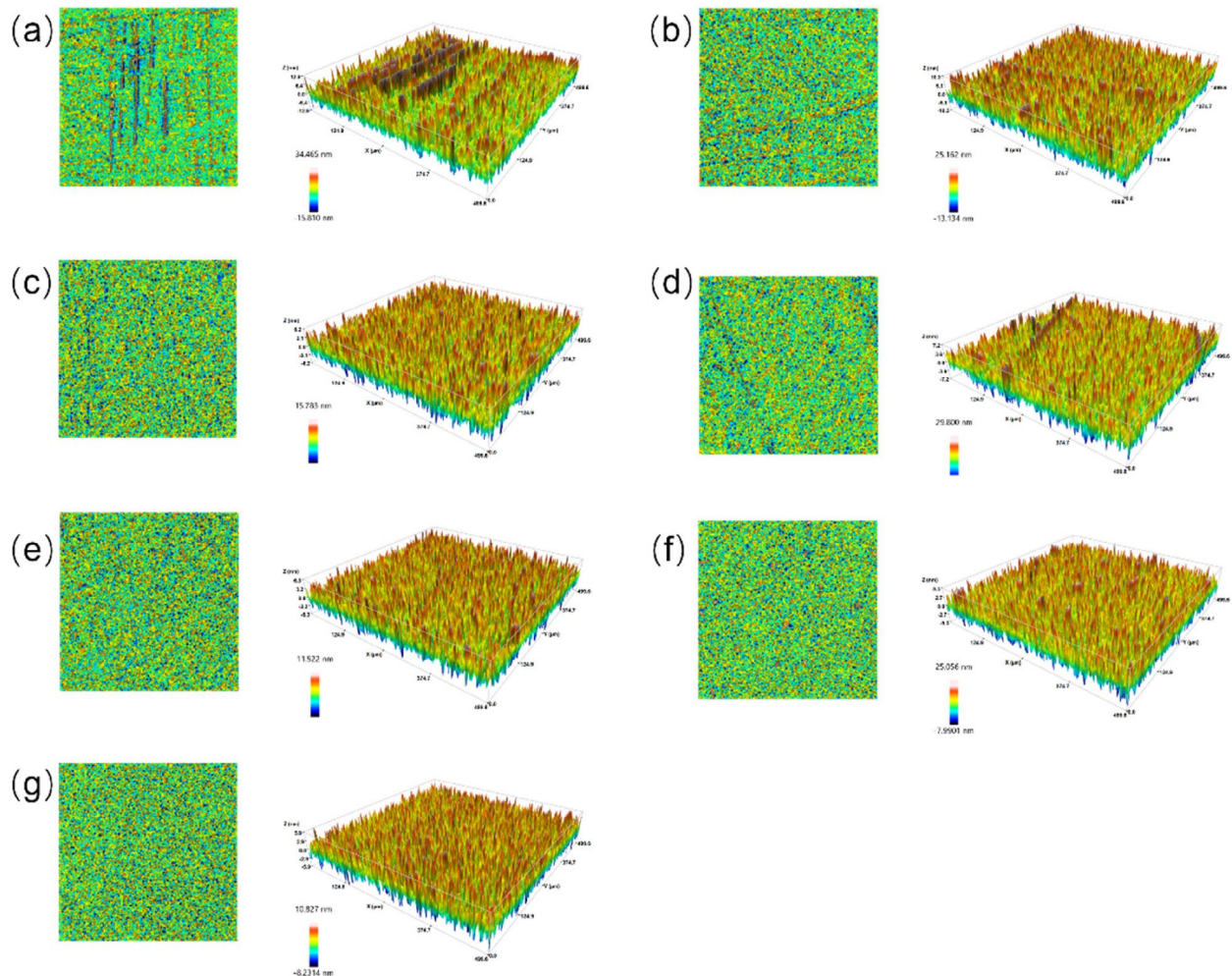


Fig. 10 Surface profiles of glass substrates: (a) unpolished, $S_a=3.12$ nm; (b-g) polished by CeO_2 and $Ce_{1-x}Nd_xO_2$: $S_a=(2.71$ nm; 1.65 nm; 1.83 nm; 1.68 nm; 1.38 nm; 1.56 nm

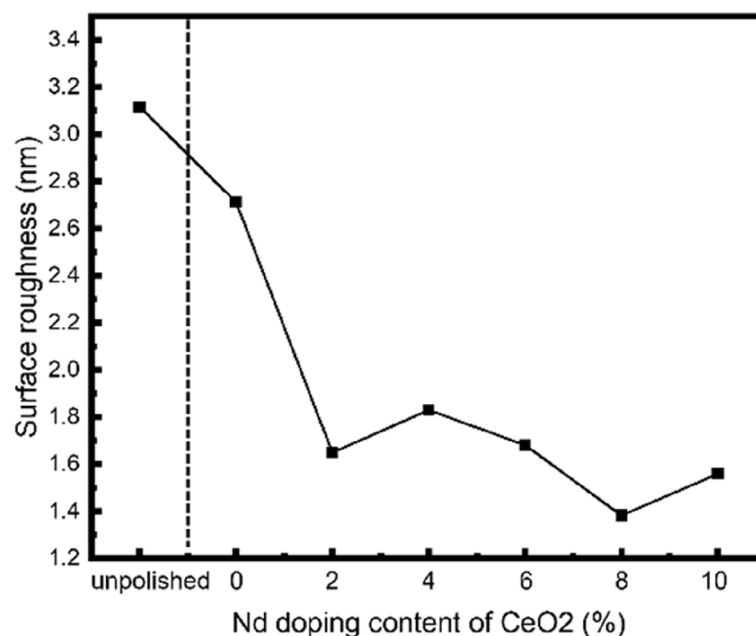


Fig. 11 Surface roughness vs. different Nd³⁺ doping contents

has the lowest surface roughness. However, according to previous experiments, the Ce³⁺ concentration of Ce_{0.92}Nd_{0.08}O₂ abrasive is not the highest, nor is the abrasive size the largest. This suggests that while the chemical and mechanical effects of Ce_{0.92}Nd_{0.08}O₂ abrasive may not be the strongest, it still achieves the lowest surface roughness. This can be attributed to a balanced synergy between chemical bonding with SiO₂ and mechanical grinding, optimizing the polishing effect. When the doping amount is increased to 8%, the particle size of cerium oxide is reduced to 303 nm, resulting in a diminished mechanical effect. At this doping level, the Ce³⁺ content on the surface is 34.63%, and the chemical bonding is less pronounced. During the polishing process, the cerium oxide abrasive particles predominantly bond to the rough peaks and are then removed via mechanical action. Due to the smaller particle size, the wear particles are less likely to scratch the substrate during the mechanical removal process. As a result, the rough peaks are effectively removed without causing scratches on the flat areas, leading to the lowest surface roughness observed.

When the doping amount is 4%, the Ce_{0.96}Nd_{0.04}O₂ abrasive exhibits the highest surface Ce³⁺ concentration, indicating the strongest chemical activity. However, glass substrates polished with polishing slurries prepared by Ce_{0.96}Nd_{0.04}O₂ abrasive show the highest surface roughness. This is primarily due to two factors. First, the strong chemical interaction between the abrasive and SiO₂ leads to a strong bond, causing residual Ce_{0.96}Nd_{0.04}O₂ on the substrate surface. This adhesive effect results in

the abrasive particles sticking to the substrate material, which increases surface roughness. Second, the increase in Ce³⁺ content facilitates the bonding and removal of both rough peaks and flat areas. The removal of flat regions leads to the formation of grooves, further increasing the surface roughness. Additionally, although the particle size of the wear particles decreases to approximately 400 nm, reducing the mechanical action, the particles exhibit an octahedral morphology, which enhances the mechanical effect due to sharper edges and angles that generate higher local pressure. This allows for more effective removal of rough peaks. However, the combination of abrasive particle adhesion and over-polishing leads to an overall increase in surface roughness. For CeO₂ abrasive, although its morphology is a polyhedron, which is the least likely to cause surface scratches among the abrasive particles in this series, the amount of SiO₂ bonding is too small to effectively remove SiO₂ debris from the glass substrate. In this case, mechanical action outweighs chemical action, leading to inefficient removal of the rough peaks and consequently high surface roughness after polishing.

3.7 CMP mechanism analysis

From a microscopic perspective, as shown in Fig. 12(a) and (b), Nd³⁺ doping leads to the reduction of Ce⁴⁺ of CeO₂ abrasive. To balance the electrical and stress effects of doping [30], some Ce⁴⁺ is converted into Ce³⁺, forming oxygen vacancies [31]. Consequently, the Ce³⁺ concentration and oxygen vacancy content on the

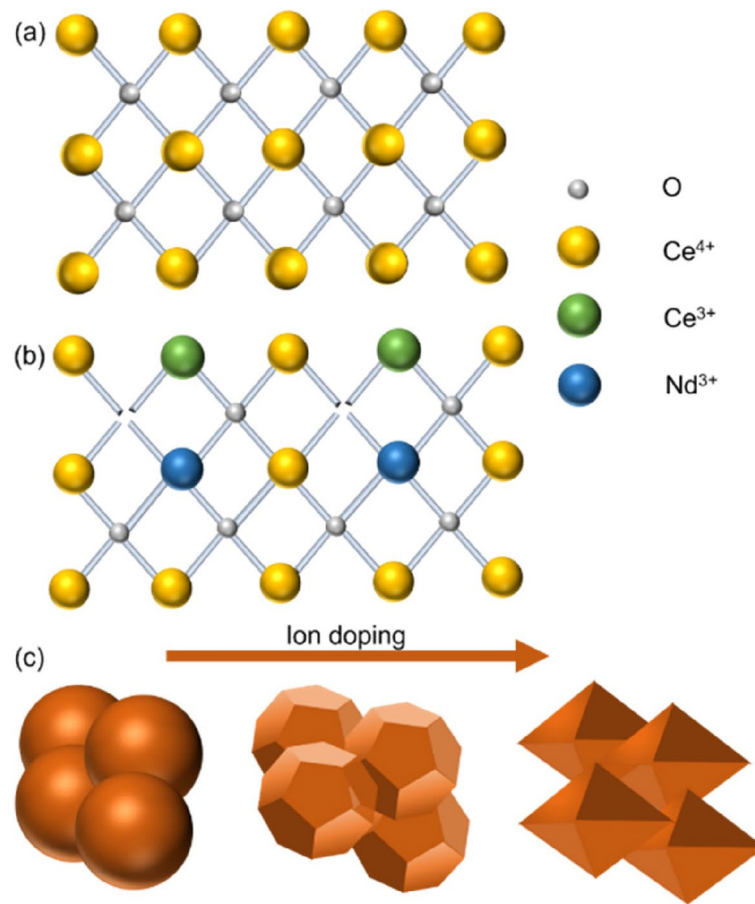
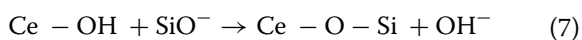


Fig. 12 a Atomic structure of pure CeO_2 and (b) Nd-doped CeO_2 surfaces and (c) the shape changes of abrasive particles caused by doping

$\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$ abrasives surface increase. On a larger scale, as shown in Fig. 12(c), Nd^{3+} doping causes the abrasives to transition from a polyhedral to an octahedral shape and reduces their size. This alteration changes both the interaction pattern and the contact frequency during polishing.

Figure 13 illustrates a schematic of the mechanism of CMP for a glass substrate using CeO_2 abrasive. Abrasives are dispersed within the polishing pad and come into contact with the glass substrate, performing both chemical and mechanical roles [32]. Specifically, the chemical action involves the bonding between the Si–O–site of the glass substrate, post-water corrosion, and the Ce–OH on the CeO_2 surface, as represented by Eq. (7). Simultaneously, under the mechanical action exerted by polishing pads and abrasive particles, Si–O–Si bonds with relatively weak bonding strength are more likely to break, allowing SiO_2 debris to be taken away [33].



Ce^{3+} of CeO_2 enhances the chemical interaction between CeO_2 and SiO_2 [18, 21, 31], leading

to increased formation of Ce–O–Si bonds forming, which facilitates the removal of more SiO_2 fragments and thereby improves the MRR during polishing. The mechanical aspect involves the abrasive particles grinding the softened layer. As shown in Fig. 13, the abrasive particles, driven by the polishing pad, grind the rough peaks on the softened glass surface to achieve smoothness. However, due to the unique groove structure of the polishing pad, some smaller abrasives are trapped in the grooves and cannot make contact with the glass substrate surface, rendering them ineffective. Additionally, the effective area of direct contact between larger abrasive and the glass substrate surface increases, and the larger abrasives exert a greater local load on the substrate, typically resulting in lower polishing quality [34]. When the abrasive particles are polyhedral, the grinding mode is rolling, whereas with octahedral particles, the grinding mode is sliding. This sliding mode creates greater local pressure, making material removal easier but also increasing the risk of surface scratching [35]. Therefore, when either the chemical or mechanical effects are too strong, the Sa increases.

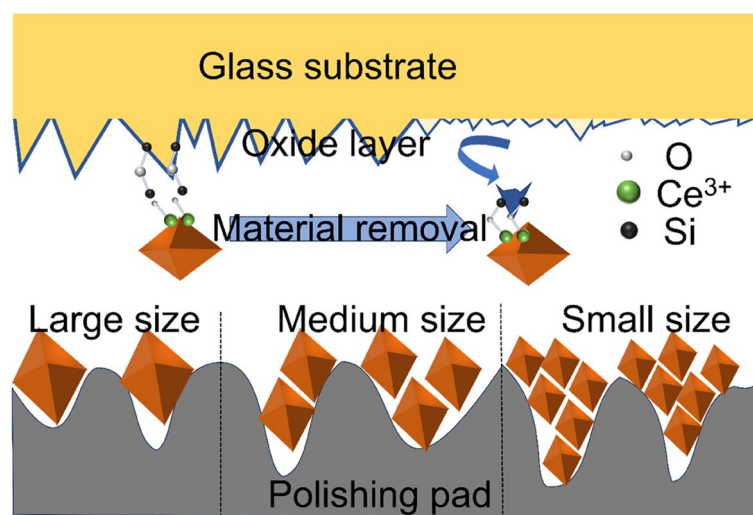


Fig. 13 CMP mechanism diagram

Only when the two effects are balanced and optimally coordinated will the Sa reach its lowest point.

4 Conclusion

1. Nd³⁺-doped cerium oxide was successfully synthesized using the salt melting method. The doped cerium oxide exhibits higher surface Ce³⁺ content and smaller particle size. Additionally, the morphology transitions from polyhedral to octahedral.
2. The Ce³⁺ concentration on the surface of cerium oxide initially increases and then decreases with increasing Nd³⁺ content. The increase in Ce³⁺ content reduces the contact angle of the polishing slurry, enhancing the effective contact between the abrasive particles and the substrate. This leads to improvements in both the chemical and mechanical effects during the polishing process.
3. With the increase in Nd³⁺ doping, the particle size of cerium oxide decreases, which leads to a reduction in the mechanical effect due to the smaller particle size.
4. Nd³⁺ doping causes the cerium oxide morphology to shift from polyhedral to octahedral. The octahedral shape, with its sharper edges and angles, generates higher local pressure during polishing, which increases the friction coefficient and enhances the mechanical action in the polishing process.
5. At an 8% doping level, a balance between chemical and mechanical effects is achieved, resulting in the lowest surface roughness.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1007/s44251-025-00072-x>.

Supplementary Material 1.

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Authors' contributions

CRedit authorship contribution statement. Yesheng Zhang: Writing – original draft, Project administration, Methodology, Investigation. Hong Lei: Writing – review & editing. Liqiang Luo: Formal Analysis, Supervision. Jianhua Zhang: Formal Analysis, Supervision.

Data availability

Data available on request from the authors.

Declarations

Competing interests

No conflict of interest exists in the submission of this manuscript, and the manuscript is approved for publication by all the authors concerned. I would like to declare on behalf of my co-authors that the work described is original research that has not been published previously, and is not currently under consideration for publication elsewhere, in whole or in part. All the authors listed have approved the manuscript that is enclosed.

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